

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

United States Patent and Trademark
Office
(Box PCT)
Crystal Plaza 2
Washington, DC 20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 12 June 1997 (12.06.97)	
International application No. PCT/BE95/00106	Applicant's or agent's file reference V 358.168
International filing date (day/month/year) 17 November 1995 (17.11.95)	Priority date (day/month/year)
Applicant WU, Xiao et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

17 May 1997 (17.05.97)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Marie-José Devillard
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY 11 JUIN 1997

PCT

From the INTERNATIONAL BUREAU

NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

To:

SCHMITZ, Y.
Gevers Patents
Holidaystraat 5
B-1831 Diegem
BELGIQUE

Date of mailing (day/month/year) 29 May 1997 (29.05.97)		
Applicant's or agent's file reference V 358.168		IMPORTANT NOTICE
International application No. PCT/BE95/00106	International filing date (day/month/year) 17 November 1995 (17.11.95)	Priority date (day/month/year)
Applicant VRIJE UNIVERSITEIT BRUSSEL et al		

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:

AU, BR, CA, CN, CZ, DE, EP, FI, JP, KP, KR, NO, PL, RO, SK, US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

AL, AM, AP, AT, BB, BG, BY, CH, DK, EE, ES, GB, GE, HU, IS, KE, KG, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NZ, OA, PT, RU, SD, SE, SG, SI, TJ, TM, TT, UA, UG, UZ, VN

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on 29 May 1997 (29.05.97) under No. WO 97/19033

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a **demand for international preliminary examination** must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the **national phase**, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer J. Zahra
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 730.91.11

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PATENT COOPERATION TREATY

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REC'D 18 FEB 1998

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference V716579/V358168	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (PCT/IPEA/416)	
International application No. PCT/BE95/00106	International filing date (day/month/year) 17/11/1995	Priority date (day/month/year) 17/11/1995 NONE
International Patent Classification (IPC) or national classification and IPC C04B28/34		
Applicant VRIJE UNIVERSITEIT BRUSSEL et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.



- ☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 4 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

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GROUP 1300

Date of submission of the demand 17/05/1997	Date of completion of this report 16.02.98
Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer Hoyer, W Telephone No. (+49-89) 2399-8439 

INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

International application No. PCT/BE95/00106

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-24 as originally filed

Claims, No.:

1-27 as received on 30/08/1997 with letter of 27/08/1997

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

see separate sheet

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	13,15,18,23,24
	No:	Claims	1-12,14,16,17,19-22,25-27
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-27
Industrial applicability (IA)	Yes:	Claims	1-27
	No:	Claims	

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/BE95/00106

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

I.3. Amendments beyond the disclosure as filed

The feature "strongly acidic" introduced into claim 1, 19 and 20 could not be traced or unambiguously derived from the originally filed documents, at least not in its broadest possible interpretation. It is derivable that component A is prepared in the presence of an aqueous solution containing phosphoric acid (cf. p. 6, ultimate paragraph or claim 19). However, the extent of the term "strongly acidic aqueous solution" is, without reference, undefined as to any pH below 7 and includes furthermore the presence of acids, such as nitric or sulfuric acid which are not disclosed. Thus the amendments of claims 1, 19 and 20 are not considered in this report.

V. Novelty and inventive step

1. Reference is made to the following documents:

D1 = DE-A-23 56 524

D2 = GB-A-2 100 246

- 1.1 A product comprising phosphate, an oxy-boron compound and wollastonite is already known. D1 discloses in claims 1, 2, 5 and 6 an aqueous dispersion suitable as binder, i.e. "an inorganic resin", comprising a 30 to 50 % solution of phosphates, in particular, alkali and/or aluminum phosphates, borates, e.g. ulexite (NaCa-borate) and silicate minerals, in particular, wollastonite. In this connection, aluminum phosphate is mentioned in the present application as suitable phosphate (cf. p. 3, line 29). D1 discloses also the application of NaPO_3 which has a pH of 6 in a 1 % aqueous solution (cf. D1, p. 6, lines 13 - 15). D1 refers to wollastonite as a preferred material of superior quality. Various other metal phosphates and borates are possible (cf. pages 5 and 6). Optionally, a pigment can be present (cf. claim 4). Claim 5 refers to a dispersion of 50 wt.% AlPO_4 and 50 wt.% wollastonite. Claim 6 which reads on claim 3 claims a ratio of borate to mineral of 78:14. According to p. 7, ultimate paragraph, the binder can be prepared from a mixture of 55 - 73 wt.% mineral, 25 to 45 % borate and/or phosphate glass, optionally alumina-containing material ("tonerdehaltiges Material" which is considered to be a filler), and water at 200 °C. Moreover, rock-forming material, e.g. basalt may be

used as fillers (cf. p. 9, 2nd paragraph). Rock-forming materials contain silicate which are considered as "derivatives" of silica. The formation of an "at least semi-transparent solution" appears to be the inevitable result of the process in D1. Sodium carbonate may be present which acts as foaming agent ("Treibmittel"; cf. p. 6, 2nd paragraph). The use of the binder to produce shaped bodies is disclosed at p. 9, 2nd paragraph. Those bodies are considered to be "prepreg products". The setting process ("aushärten") takes place between 200 and 600 °C. Consequently, the setting is retarded below these temperatures. It appears to be self-evident that the supporting surface must be made from of metal, organic, or inorganic, i.e. any material.

- 1.2 The disclosure of D1 is considered to be novelty-destroying for claims 1 - 12, 14, 16, 17, 20 - 22 and 25 - 27.
- 1.3 A process as claimed in claim 19, namely a process to prepare component A as defined in claim 1 which comprises mixing of a metal and/or metal oxide and/or metal phosphate including hydrates and derivatives in phosphoric acid solution is known from D2 (cf. for instance the examples). The formation of an "at least semi-transparent solution" appears to be the inevitable result. D2 corresponds to US-A-4 375 516 which is acknowledged as prior art in the application.
- 1.4 Claims 13, 15, 18, 23 and 24 seem to refer merely to design-features. The use of silica, its derivatives or fibers as filler or reinforcement materials appears to be an entirely conventional measure in the art. The same applies for the use of zinc stearate which appears to be a conventional surfactant. As regards the particle sizes and aspect ratio of the wollastonite claimed in claim 13 it appears to be obvious that fibrous wollastonite has better reinforcement capabilities and is thus preferred.
- 1.5 According to the comments above, claims 1 - 27 do not meet the requirements of Art. 33(2) and/or (3) PCT.

VII. Typographical error

At p. 7, line 7 "phosphorous" reads better "phosphorus".

VIII. Clarity

1. The general statement in the description at page 20, line 13 ("spirit of the invention") is not clear, and when used to interpret the claims renders them also unclear, contrary to Article 6 PCT.

Claims

1. An inorganic resin composition which comprises, in combination, a strongly acidic aqueous solution of metal phosphate (component A), an oxy-boron compound (component B) and a wollastonite compound (component C).

2. A composition according to claim 1 wherein the metal phosphate is selected from the group consisting of aluminium phosphates, zirconium phosphates, magnesium phosphates, zinc phosphates, calcium phosphates, iron phosphates, including derivatives and mixtures thereof.

3. A composition according to claim 1 or 2 wherein said oxy-boron compound is selected from the group consisting of boric acid, alkali metal and alkaline-earth metal salts of boric acid, amine and ammonium salts of boric acid, including hydrates and mixtures thereof.

4. A composition according to claim 3 wherein said oxy-boron compound is selected from the group consisting of boric acid, sodium borate, ammonium borate, calcium borate, including hydrates and mixtures thereof.

5. A composition according to claim 3 or 4 wherein said oxy-boron compound is as a powder or a liquid.

6. A composition according to claim 1 wherein said wollastonite compound is a natural or synthetic wollastonite, in calcined or non-calcined state, or a combination thereof.

7. A composition according to any one of claims 1 to 6 wherein said component A comprises, per 100 parts by weight of said wollastonite compound calculated on a basis of pure calcium silicate:

the equivalent of 14 to 135 parts by weight of phosphorous pentoxide contained in said metal phosphate, and the equivalent of 2 to 65 parts by weight of metal oxide contained in said metal phosphate.

8. A composition according to claim 7 wherein said component A comprises:

the equivalent of 24 to 86 parts by weight of phosphorous pentoxide, and

the equivalent of 5 to 47 parts by weight of metal oxide.

5 9. A composition according to any one of claims 1 to 8 wherein the whole water content of the composition is from 8 to 150 parts by weight per 100 parts by weight of said wollastonite compound calculated on a basis of pure calcium silicate.

10 10. A composition according to claim 9 wherein the whole water content of the composition is from 11 to 95 parts by weight.

15 11. A composition according to any one of claims 1 to 10 wherein said oxy-boron compound is present, calculated on an anhydrous basis, in an amount of 0.2 to 50 parts by weight per 100 parts by weight of said wollastonite compound calculated on a basis of pure calcium silicate.

20 12. A composition according to claim 11 wherein said oxy-boron compound, calculated on an anhydrous basis, is present in an amount of 2 to 20 parts by weight.

 13. A composition according to any one of claims 6 to 12 wherein the particle size and the aspect ratio of the wollastonite are not larger than 150 μ m and 10 respectively.

25 14. A composition according to any one of the claims 1 to 13 which comprises at least additives such as fibres, a filler, a foaming agent, a surfactant, and a pigment, used either alone or in combination thereof.

30 15. A composition according to claim 14 wherein said surfactant is zinc stearate.

 16. A composition according to claim 14 or 15 wherein said foaming agent is a carbonate selected from the group consisting of calcium carbonate, magnesium carbonate, sodium carbonate, potassium carbonate, used either as powder
35 or aqueous solution, or a combination thereof.

17. A composition according to any one of claims 14 to 16 wherein said filler is silica or a derivative thereof.

5 18. A composition according to any one of claims 14 to 17 wherein said fibre is selected from the group consisting of metal fibre, organic fibre, and inorganic fibre including glass fibre.

19. A process for preparing said strongly acidic aqueous solution of metal phosphate of said composition according to
10 any one of claims 1 to 18 which comprises mixing metal and/or metal oxide and/or metal phosphate including hydrates and derivatives thereof in phosphoric acid aqueous solution at a temperature and for a time sufficient to form at least a semi-transparent solution.

15 20. A process for preparing a product of the inorganic resin composition according to any one of claims 1 to 19, which comprises:

mixing said strongly acidic aqueous solution of metal phosphate with said oxy-boron compound at a temperature and for a time
20 sufficient to form an aqueous solution, and

contacting said wollastonite compound and optionally one or more of said additives with the above solution to form a slurry, and

bringing said slurry on a surface capable of at least
25 partially supporting said slurry wherein said slurry reacts to set as a shaped product of the inorganic resin composition.

21. A process for preparing a prepreg product of said inorganic resin composition according to any one of
30 claims 1 to 19, which comprises:

mixing said component A, said component B, said component C and optionally one or more of said additives to form a slurry, and

impregnating fibres with said slurry, and

keeping the impregnated fibres, which is called prepreg, at a temperature sufficiently low to prevent any setting reaction, and

bringing said prepreg on a surface capable of supporting
5 said prepreg wherein the slurry reacts to set as a shaped product of said prepreg.

22. A process according to claim 20 or 21 wherein said slurry is kept at a temperature sufficiently low to retard any setting reaction before being brought on
10 said supporting surface.

23. A process according to any one of claims 20 to 22 wherein said supporting surface comprises fibres including inorganic, organic and/or metallic fibres.

24. A process according to any one of claims 20
15 to 23 wherein said slurry impregnates said fibres of said supporting surface to form a fibre reinforced product.

25. A process according to any one of claims 20 to 22 wherein said supporting surface is made of metal, organic, or inorganic material.

20 26. Use of an inorganic resin composition according to any one of claims 1 to 19 and/or a shaped product of the inorganic resin composition prepared by the process according to any one of claims 20 to 25, as a binder, coating, surfacing agent, adhesive, cementing agent.

25 27. Use according to claim 26 wherein the shaped product has a foamed structure.

Abstract

In a method for the frequency analysis of a signal of a hazard detector a wavelet transformation (1) is combined
5 with fuzzy logic analysis. In the transformation by means of an orthonormal or semi-orthonormal wavelet, the original signal $(x_{0,k})$ is fed to a multi-stage filter cascade of pairs of high-pass/low-pass filters (HP, LP). In each filter stage an association function (μ_i) is produced from the
10 results of the high-pass filter, wavelet coefficients and values of the original signal $(x_{0,k})$. These functions are normalised and are used in this form for further analysis (2) in accordance with fuzzy logic rules.

15 The method is particularly suitable for the analysis of output signals of hazard detectors such as flame detectors, noise detectors and the like. The wavelet transformation (1) and fuzzy logic analysis (2) are performed by a small number of lines of processor code, whereby the analysis can
20 be carried out using a cost-effective processor and is speeded up with equal or improved accuracy.

PATE COOPERATION TREATY

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference V 358.168	<div style="display: flex; justify-content: space-between;"> <div style="text-align: center;">FOR FURTHER ACTION</div> <div style="font-size: 0.8em;">see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</div> </div>	
International application No. PCT/BE 95/00106	International filing date (day/month/year) 17/11/95	(Earliest) Priority Date (day/month/year)

Applicant

VRIJE UNIVERSITEIT BRUSSEL et al.

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. ☐ Certain claims were found unsearchable (see Box I).

2. ☐ Unity of invention is lacking (see Box II).

3. ☐ The international application contains disclosure of a nucleotide and/or amino acid sequence listing and the international search was carried out on the basis of the sequence listing

☐ filed with the international application.

☐ furnished by the applicant separately from the international application,

☐ but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.

☐ Transcribed by this Authority

4. With regard to the title, ☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

Inorganic resin compositions, their preparation and use thereof.

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is:

Figure No. --- ☐ as suggested by the applicant.

☐ None of the figures.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/BE 95/00106

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C04B28/34 //(C04B28/34,14:04,20:00,24:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,23 56 524 (C. WÜSTEFELD) 28 May 1975 see page 5, line 31 - page 6, line 3 see page 7, line 16 - page 8, line 13 see claims 1,4-6,11 ---	1-6,14, 26
A	DE,A,30 43 856 (ZSCHIRMER & SCHWARZ) 3 June 1982 see claims 1-5 ---	1-5,14, 17,26
A	FR,A,2 291 951 (W.R.GRACE & CO.) 18 June 1976 see page 2, line 10 - line 28 see claims 1,3,4 --- -/--	1-5,14, 17,26



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

4 July 1996

Date of mailing of the international search report

2 2. 07. 96

Name and mailing address of the ISA

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Authorized officer

Puetz, C

INTERNATIONAL SEARCH REPORT

International Application No

PCT/BE 95/00106

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 792 359 (BARRALL ET AL.) 20 December 1988 cited in the application see the whole document ---	1,2,6, 14, 17-19,26
A	GB,A,2 100 246 (ARMSTRONG WORLD INDUSTRIES) 22 December 1982 cited in the application see the whole document ---	1,2,6, 14, 16-19, 26,27
A	US,A,3 804 651 (SEMLER) 16 April 1974 cited in the application see the whole document ---	1,2,6,26
A	CHEMICAL ABSTRACTS, vol. 99, no. 26, 26 December 1983 Columbus, Ohio, US; abstract no. 217480k, HITACHI CHEMICAL CO.: "inorganic binder for mica plate manufacture" page 312; XP000185962 see abstract & JP,A,58 130 160 ---	1-5,14, 16,26
A	CHEMICAL ABSTRACTS, vol. 113, no. 22, 26 November 1990 Columbus, Ohio, US; abstract no. 194440p, ZHOU WENBIN: "inorganic binder for manufacturing mica sheets" page 180; XP000192580 see abstract & CN,A,1 034 381 (FAMING ZHUANLI SHENQING GONGKAI SHUOMINGSHU) -----	1-5,14, 26

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/BE 95/00106

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-2356524	28-05-75	NONE	
DE-A-3043856	03-06-82	NONE	
FR-A-2291951	18-06-76	US-A- 3960580	01-06-76
		CA-A- 1072586	26-02-80
		DE-A- 2551140	26-05-76
		GB-A- 1512275	24-05-78
		JP-A- 51076320	01-07-76
		SE-B- 408055	14-05-79
		SE-A- 7513029	24-05-76
US-A-4792359	20-12-88	NONE	
GB-A-2100246	22-12-82	US-A- 4375516	01-03-83
		AU-B- 544513	30-05-85
		AU-B- 8466582	23-12-82
		BE-A- 893504	01-10-82
		CA-A- 1186130	30-04-85
		DE-A- 3222078	24-02-83
		FR-A,B 2507591	17-12-82
		JP-C- 1604592	13-05-91
		JP-B- 2028547	25-06-90
		JP-A- 58002272	07-01-83
		LU-A- 84193	13-12-82
		NL-A- 8202362	17-01-83
		SE-B- 455194	27-06-88
		SE-A- 8203688	17-12-82
		US-E- RE33366	02-10-90
US-A-3804651	16-04-74	NONE	

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Claims

1. An inorganic resin composition which comprises, in combination, an aqueous solution of metal phosphate (component A), an oxy-boron compound (component B) and a wollastonite compound (component C).
2. A composition according to claim 1 wherein the metal phosphate is selected from the group consisting of aluminium phosphates, zirconium phosphates, magnesium phosphates, zinc phosphates, calcium phosphates, iron phosphates, including derivatives and mixtures thereof.
3. A composition according to claim 1 or 2 wherein said oxy-boron compound is selected from the group consisting of boric acid, alkali metal and alkaline-earth metal salts of boric acid, amine and ammonium salts of boric acid, including hydrates and mixtures thereof.
4. A composition according to claim 3 wherein said oxy-boron compound is selected from the group consisting of boric acid, sodium borate, ammonium borate, calcium borate, including hydrates and mixtures thereof.
5. A composition according to claim 3 or 4 wherein said oxy-boron compound is as a powder or a liquid.
6. A composition according to claim 1 wherein said wollastonite compound is a natural or synthetic wollastonite, in calcined or non-calcined state, or a combination thereof.
7. A composition according to any one of claims 1 to 6 wherein said component A comprises, per 100 parts by weight of said wollastonite compound calculated on a basis of pure calcium silicate:
- the equivalent of 14 to 135 parts by weight of phosphorous pentoxide contained in said metal phosphate, and the equivalent of 2 to 65 parts by weight of metal oxide contained in said metal phosphate.
8. A composition according to claim 7 wherein said component A comprises:

- 25 -

the equivalent of 24 to 35 parts by weight of phosphorous pentoxide, and

the equivalent of 5 to 47 parts by weight of metal oxide.

5 9. A composition according to any one of claims 1 to 8 wherein the whole water content of the composition is from 8 to 150 parts by weight per 100 parts by weight of said wollastonite compound calculated on a basis of pure calcium silicate.

10 10. A composition according to claim 9 wherein the whole water content of the composition is from 11 to 95 parts by weight.

15 11. A composition according to any one of claims 1 to 10 wherein said oxy-boron compound is present, calculated on an anhydrous basis, in an amount of 0.2 to 50 parts by weight per 100 parts by weight of said wollastonite compound calculated on a basis of pure calcium silicate.

20 12. A composition according to claim 11 wherein said oxy-boron compound, calculated on an anhydrous basis, is present in an amount of 2 to 20 parts by weight.

13. A composition according to any one of claims 6 to 12 wherein the particle size and the aspect ratio of the wollastonite are not larger than 150 μ m and 10 respectively.

25 14. A composition according to any one of the claims 1 to 13 which comprises at least additives such as fibres, a filler, a foaming agent, a surfactant, and a pigment, used either alone or in combination thereof.

30 15. A composition according to claim 14 wherein said surfactant is zinc stearate.

16. A composition according to claim 14 or 15 wherein said foaming agent is a carbonate selected from the group consisting of calcium carbonate, magnesium carbonate, sodium carbonate, potassium carbonate, used either as powder
35 or aqueous solution, or a combination thereof.

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17. A composition according to any one of claims 14 to 16 wherein said filler is silica or a derivative thereof.

5 18. A composition according to any one of claims 14 to 17 wherein said fibre is selected from the group consisting of metal fibre, organic fibre, and inorganic fibre including glass fibre.

10 19. A process for preparing said aqueous solution of metal phosphate of said composition according to any one of claims 1 to 18 which comprises mixing metal and/or metal oxide and/or metal phosphate including hydrates and derivatives thereof in phosphoric acid aqueous solution at a temperature and for a time sufficient to form at least a semi-transparent solution.

15 20. A process for preparing a product of the inorganic resin composition according to any one of claims 1 to 19, which comprises:

20 mixing said aqueous solution of metal phosphate with said oxy-boron compound at a temperature and for a time sufficient to form an aqueous solution, and

contacting said wollastonite compound and optionally one or more of said additives with the above solution to form a slurry, and

25 bringing said slurry on a surface capable of at least partially supporting said slurry wherein said slurry reacts to set as a shaped product of the inorganic resin composition.

30 21. A process for preparing a prepreg product of said inorganic resin composition according to any one of claims 1 to 19, which comprises:

mixing said component A, said component B, said component C and optionally one or more of said additives to form a slurry, and

impregnating fibres with said slurry, and

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keeping the impregnated fibres, which is called prepreg, at a temperature sufficiently low to prevent any setting reaction, and

bringing said prepreg on a surface capable of supporting
5 said prepreg wherein the slurry reacts to set as a shaped product of said prepreg.

22. A process according to claim 20 or 21 wherein said slurry is kept at a temperature sufficiently low to retard any setting reaction before being brought on
10 said supporting surface.

23. A process according to any one of claims 20 to 22 wherein said supporting surface comprises fibres including inorganic, organic and/or metallic fibres.

24. A process according to any one of claims 20
15 to 23 wherein said slurry impregnates said fibres of said supporting surface to form a fibre reinforced product.

25. A process according to any one of claims 20 to 22 wherein said supporting surface is made of metal, organic, or inorganic material.

20 26. Use of an inorganic resin composition according to any one of claims 1 to 19 and/or a shaped product of the inorganic resin composition prepared by the process according to any one of claims 20 to 25, as a binder, coating, surfacing agent, adhesive, cementing agent.

25 27. Use according to claim 26 wherein the shaped product has a foamed structure.

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(57) Abstract Inorganic resin compositions comprising, in combination, an aqueous solution of metal phosphate, an oxy-boron compound, a wollastonite compound and other optional additives, inorganic composite articles and products reinforced by fillers and fibres including glass fibres obtained from these compositions and processes for preparing said products.			

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INORGANIC RESIN COMPOSITIONS, THEIR PREPARATION AND USE THEREOF

Background of the invention

5

Technical field

This invention relates to inorganic resins in composition of aqueous solution of inorganic metal phosphate, oxy-boron compound and wollastonite compound; to various additives for said composition; to processes for forming said resin and the resin product; to products manufactured by said resin composition and said process. The unique feather of this invention is that pot life of the fresh resin and temperature increase of the resin during setting reaction can be controlled so that its pot life can be between few minutes to an order of magnitude of several hours or longer; whereas hardened resin and resin product have good material properties and wide range of use. Both cellular and non cellular structures can be obtained.

20

The resin of the present invention can be used as adhesives and binders. In terms of properties, inorganic resin of the present invention and its products lies between those such as e.g. Portland cement and those such as e.g. technical ceramics. Fresh mixture of the resin has low viscosity, is storable at low temperatures and easy to use; while the hardened resin is strong, durable, resistant against mild acid attack, fire-proof, and stable at high temperatures. It is suitable to make, such as but not limited, adhesives, binders, coatings and inorganic composites reinforced by fillers and fibres including all glass fibres, used both at low and high temperatures.

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Description of the related art

Wollastonite has been employed not long time ago as primary material in phosphate cement compositions. Only few formulations are known in that field so far, they all have quick setting characteristics. Hardening of these compositions usually occurs at ambient condition in a range from several minutes to ca 10-20 minutes after forming of the cement, which is practically impossible to be used in applications such as that of composite materials. Large amount of heat production is another typical phenomenon of the traditional phosphate cements which may produce defects inside of the material and affects negatively on material properties. When wollastonite is employed as primary material in the composition, the quick setting may result in extra voids and cracks in structure of the material due to formation of CO₂ during the setting process produced by decomposition of calcite (CaCO₃) contained in the wollastonite, which further undermines strength and durability of the material. US Pat. No. 3,804,651 dated Apr. 16, 1974 to C.E. Semler discloses a quick setting gel binder of phosphate solutions and wollastonite. The cured binder shows a good mechanical strength and durability, but its fresh mixture gels quickly and is claimed as a quick setting composition. US Pat. No. 4,375, 516 dated Mar. 1, 1983 to Jeffery L., Barrall et.al discloses a material in composition of aluminium phosphate solution and solid component containing wollastonite. This composition usually sets in several minutes in the temperature range of 4-25°C. US Pat. No. 4,792,359 dated Dec. 20, 1988 to Jeffery L., Barrall et.al discloses a method to prepare composite materials by hot pressing the mixture of phosphate cement and varies fibres at about 85°C under pressures, which takes advantage of the quick setting.

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As a summary, these inorganic phosphate compositions are found not related to this invention. In terms of composition, no oxy-boron compound is used to extend pot life of these phosphate cement compositions; in terms of setting time, all available compositions has a quick setting; in terms of pot life during which period the mixture keeps flowable, no information is available probably due to the quick setting; in terms of application, all available compositions is used for purposes which needs quick setting.

The inorganic resins of the present invention have a controllable pot life and temperature increase in its fresh state; and have good material properties for the hardened resin, such as, e.g., good mechanical strength, durability, resistance against mild acid attack, high scratch hardness, non flammability, high temperature resistance, and good adhesion with other materials such as fibres including glass fibres,

20

Summary of the invention

The inorganic resins of the present invention are formed basically by reactions between three components, either physically separated or mixed or in combination thereof. The component A is an aqueous solution of metal phosphate preferably selected from the group consisting of aluminium phosphates, zirconium phosphates, magnesium phosphates, zinc phosphates, calcium phosphates, iron phosphates, including derivatives and mixtures thereof. It should be understood that the term solution of the component A is used broadly herein to include aqueous reaction mixtures, and the term derivative of metal phosphates herein includes all types of phosphate such as polyphosphate and dihydrogen phosphate. The component B comprises oxy-boron

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compound including its hydrates. The component C comprises wollastonite compound. Fillers and fibres including glass fibres can be introduced to the inorganic resin of this invention to improve material properties. Cellular
5 structures of the inorganic resin can be produced by employing foaming agents and surfactants.

Being formed by contacting all ingredients together by way of such as intermixing, fresh resin of this
10 invention has an adjustable pot life in the range from several minutes to an order of magnitude of several hours or longer, and correspondingly a setting time from few minutes to several hours or longer at ambient temperatures; has a controlled temperature increase during setting reaction;
15 while the hardened resin has very good material properties. The composition of the present invention interacts and is able to set without the use of externally applied heat. These compositions and their unique characteristics such as the extended pot life distinguish themselves from the other
20 traditional phosphate cements in the related field. Hardened resin of this invention has a three dimensional network structures. Due to this nature, inorganic resins of the present invention are formulated to be essentially strong, durable, resistant against environmental attack such as acid
25 rain, non flammable, and stable at high temperatures.

Inorganic resin of this invention has good adhesion with fibres, meanwhile it shows no attack against fibres including glass fibres. Accordingly qualified
30 inorganic composites can be produced by this invention. Products made by inorganic resin of this invention can replace at least a portion of presently known products based on organic resins, traditional cements and ceramics in a wide range of applications, such as, fibre reinforced
35 composite products; moulded configurations in cellular and non-cellular structures; thermal, electrical and/or

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acoustical insulations; binders and adhesives; coatings and
or surfacing agents; patching compositions and the like.
Further, the use of inexpensive materials and easy
processing compared to that of typical organic resins or
5 ceramics offers a number of advantages over many of the
organic resins and ceramics destined for similar
applications.

It is therefore one objective of the present
10 invention to provide a range of inorganic resin compositions
with the above mentioned features and advantages.

Another objective of the present invention is to
provide processes to prepare these resin compositions and
15 resin products, as well as the use thereof.

These and other objectives and advantages of the
present invention will become apparent from the detailed
description given hereafter by way of non limiting examples.
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Detailed description of the invention

The inorganic resins of the present invention are formed basically by reactions between three components, either physically separated or mixed or in combination thereof. The component A is an aqueous solution of metal phosphate preferably selected from the group consisting of aluminium phosphates, zirconium phosphates, magnesium phosphates, zinc phosphates, calcium phosphates, iron phosphates, including derivatives and mixtures thereof. It should be understood that the term solution of the component A is used broadly herein to include aqueous reaction mixtures, and the term derivative of metal phosphates herein includes all types of phosphate such as polyphosphate and dihydrogen phosphate. The component B comprises oxy-boron compound including its hydrates. The component C comprises wollastonite compound including natural and synthetic wollastonite, in calcined or non-calcined state. Fillers and fibres including glass fibres can be introduced to the inorganic resin of this invention to improve material properties. Cellular structures of the inorganic resin can be produced by employing foaming agents and surfactants. Having homogeneously mixed, the said components interact in a controlled way so that designed pot life and setting time can be obtained. Setting process of said inorganic resin is in general exothermic, but the temperature increase of the resin during the reaction can be controlled. Inorganic resin of this invention may set at ambient temperatures to form a strong, durable monolithic mass without applying external heat.

30

In accordance with this invention, the most important ingredient to prepare the component A is phosphoric acid aqueous solution including but not limited, e.g., ortho-phosphoric acid, pyro-phosphoric acid and polyphosphoric acid, used either alone or in combination

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thereof. Phosphoric acid is commercially available, with the 85 percent by weight being the most common concentration for the ortho-phosphoric acid. Other phosphorous based acids may also be satisfactory to practice the present invention, 5 providing that the overall water content of the reaction system is not too high. As a general rule, the phosphoric acid will be suitable if it contains the phosphorous, expressed as P_2O_5 , in range of 14 to 135 parts by weight with respect to 100 parts by weight of wollastonite in the 10 component C, with 24 to 86 parts by weight being preferred.

To practice the present invention, metal phosphate which is relatively insoluble in water is preferred to be used in the component A. It is found that 15 metal phosphate selected from the group consisting of aluminium phosphates, zirconium phosphates, magnesium phosphates, zinc phosphates, calcium phosphates, iron phosphates, including derivatives and mixtures thereof, is preferred. With respect to 100 parts by weight of 20 wollastonite in the component C, suitable amount of equivalent metal oxide contained in the metal phosphate, i.e., aluminium oxide, zirconium oxide, magnesium oxide, zinc oxide, calcium oxide and iron oxide, is in the range of 2 to 65 parts by weight, with 5 to 47 parts by weight being 25 preferred.

In accordance with this invention, the amount of water employed in the component A should be carefully controlled. Excessive water can convert the resin into a 30 thin mixture that will cause sedimentation of solid particles such as the wollastonite, which leads to an inferior product. Insufficient water will not wet the dry particles adequately to allow the necessary chemical reaction. The amount of water influences on concentration of 35 the reactive components and consequently affects on the pot life and setting process of the resin. The optimal amount of

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water will depend upon the very metal used in component A and the particular physical characteristics of the constituents of dry particles of this invention, e.g., absorbency, surface area, etc. However, it must be sufficient to adequately wet the dry particles, such as the wollastonite and fillers and/or fibres, to form desirable mixture. This optimal amount of water can be determined on a blend by blend basis. With respect to 100 parts by weight of wollastonite in the component C, the amount of water used can range from about 8 to 150 parts by weight, with from 11 to 95 parts by weight being preferred. The water content in the component A should include, for purposes of calculation, any water of hydration from the compounds in the component A, B and C.

15

In accordance with this invention, the component A can be basically prepared by mixing metal and/or metal oxide and/or metal phosphate including hydrates and derivatives thereof in phosphoric acid aqueous solution at a temperature and for a time sufficient to form at least a semi-transparent solution. Sometimes only a particle-liquid suspension is obtained after long time mixing due to such as impurities contained in the raw materials. A filtration process is then required to remove the undissolved portion of particles larger than 1 μm from the solution. The filtered solution can be employed to practise this invention if it contains desired amount of said ingredients. A clear solution homogeneous in molecular level without discrete particle distribution is preferred. It may be with or without color depends on the very metal employed.

In general, the component A of this invention is a mixture composed of various types of phosphate, including but not limited, i.e. orthophosphate, pyrophosphate, and polyphosphate, appeared either alone or in combination thereof. Exact distribution of the different phosphate

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structures depends on the method and raw materials employed to make the solution, and on the age of the solution. However, a transparent solution with an age of 3 months at 20°C is found generally sufficient to practice this invention by any person skilled in the art. The component A can be prepared all together as one liquid, or prepared separately and then mixed together as one liquid, or prepared separately and kept separately prior to use.

10 In accordance with this invention, the component B of this invention is composed of oxy-boron compound including its hydrates. The oxy-boron compound actively participates into the setting reaction, results in the very structure of the fresh resin of this invention with which
15 the pot life can be controlled.

The oxy-boron compound used in this invention generally comprises these boron compounds containing at least one boron-oxygen linkage, hereafter termed the oxy-boron compound. The oxy-boron compound is found specially effective in this invention in terms of producing a extended pot life, avoiding setting expansion and resin over-heating during the setting, i.e., temperature increases to more than 100°C when free water in the composition boils. These
20 compounds include, e.g., oxy acids of boron which contain one or more boron atoms such as, e.g., boric acid; salts of such acids, such as the alkali metal and alkali earth metal salts thereof, such as sodium borate, calcium borate and amine or ammonium salts thereof such as ammonium borate; and
25 ester of such acids, such as trialkoxy borate and triaryloxy borate, e.g., trimetal borate. Boron-containing starting materials which yield oxy-boron additives upon contact with phosphate solutions of the component A can be used to generate the oxy-boron compounds in situ. The preferred oxy-boron compound include boric acid, the alkali metal and
30 alkali earth salts of the boric acid such as the sodium

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borate, calcium borate including their hydrates. The oxy-boron compound can be used as a dry powder or as a solution by dissolving them in water or phosphoric acids. The amount of the component B used in the composition of this invention
5 can vary according to the degree of retardation and the temperature increase desired. Generally, with respect to 100 parts by weight of wollastonite in the component C, the amount of the oxy-boron compound in the mixture, calculated on an anhydrous basis, ranging from about 0.2 to 50 parts by
10 weight, preferably from about 2 to 20 parts by weight being suitable.

In accordance with this invention, the component C is the wollastonite compound including natural and
15 synthetic wollastonite, in calcined or non-calcined state. Usually the commercially available wollastonite is a mineral of natural calcium silicate (CaSiO_3) of acicular structure, with a theoretical composition of 48.3% CaO and 51.7% SiO_2 by weight. This wollastonite can be classified into two
20 categories of low aspect ratio and high aspect ratio. The low aspect ratio wollastonite, commonly with aspect ratio of not higher than 10, including that of about 1, is mainly used as flux and fillers in ceramic, metallurgical, construction and coating application. The high aspect ratio
25 wollastonite commonly with aspect ratio of 10-20 is used as fibres to produce effect of reinforcement. The most important properties of the wollastonite that affect behavior of the inorganic resin of the present invention are their loss on ignition (LOI), aspect ratio, granulometry,
30 and wollastonite content. Those characteristics can change from one wollastonite to another, depends on its mineral origin, geological history and processing technique to obtain the wollastonite. Setting process of the inorganic resin of the present invention is in one way or another
35 influenced by origin of the wollastonite, which broadly

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includes factors such as e.g. geological history, way of fabrication and impurities of the wollastonite.

Loss on ignition of the wollastonite is due to
5 release of CO₂ when the calcite (CaCO₃), which is intimately associated with the wollastonite, is decomposed into CO₂ and CaO at high temperatures. To practise this invention, the less amount of associated calcite that can be achieved, the better the wollastonite will be. However, for a practical
10 reason, certain amount of CaCO₃ content up to about 5 percent by weight is present in the commercially available wollastonite. High amount of the calcite contained in the wollastonite is not desired, because it will produce excessive CO₂ during mixing and reaction stage, which
15 results in internal defects and undermines mechanical strength. High calcite content of the wollastonite will also lead to a long mixing time in order to achieve a homogeneous mixture thus increase difficult for material processing. High amount of the calcite present in the composition may
20 disturb the three component reaction of this invention due to high reactivity between the calcite and the phosphate solution of the component A, which may lead to undesirable reactions and weak structures. One way to completely eliminate the calcite is to heat the commercial available
25 wollastonite in a range of 550-1000°C until the calcite decomposes to CaO and CO₂. The calcination process seems to produce no harmful effect on using the calcined wollastonite in this invention. To practice this invention, the range of the LOI value between 20-1000°C should not be more than 3
30 percent by weight. Using a mixture of calcined and non-calcined wollastonite is preferred with which the LOI value can be completely controlled.

Granulometry of the wollastonite plays an
35 important role in controlling pot life and setting time of the inorganic resins of the present invention. When the

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grain size is too small, the resin will be too reactive and lead to a short pot life. However, when the grain size is too large, only part of wollastonite is able to participate into the reaction so that the necessary constituent to form backbone of the structure is insufficient. Coarse wollastonite will also cause the particle sedimentation from the resin mixture due to its larger specific gravity (about 2.9). However, compared to traditional phosphate cement, this invention permits to use the wollastonite with relatively larger grain size due to the extended pot life, during which period the wollastonite will be decomposed to a satisfactory degree. To practice this invention, the wollastonite used as primary reactant is preferred not larger than 150 μm . The range of the particle size distribution is given in terms of having a product with preferred properties. Wollastonite with particle size larger than 150 μm may also be used in the composition as reactive fillers and/or fibres to improve properties of the resin product.

20

According to the present invention, aspect ratio of the wollastonite used as primary reactant should not be too high to avoid wollastonite fibre from entanglement during mixing which makes the mixing difficult. A preferable aspect ratio is not larger than about 10 which can produce desirable rheology and the wollastonite solubility in the solution of metal phosphate. Wollastonite content of the commercial wollastonite product is preferred to be more than 90 percent by weight. Wollastonite with aspect ratio of larger than about 10, and/or purity less than about 90 percent by weight may be included in general as reactive fillers and/or fibres to reinforce the inorganic resin of the present invention.

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In accordance with this invention, inorganic resins of the present invention can be packed and kept

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separately until prior the use in a three package system. However, a two package system is preferred which comprises a liquid phase and a solid phase. In accordance with this invention, the liquid phase may be composed of the component
5 A and the component B, the solid phase may be composed of the component C. The wollastonite compound may also be partially mixed with the component A, or with the mixture of the component A and component B. The remaining portion of the wollastonite compound is kept separately until prior the
10 use. To practise this two package system, mixing of the component A and the component B can be performed at a temperature and for a time sufficient to form an aqueous solution wherein the oxy-boron compounds are dissolved and incorporated in said metal phosphate. Sometimes a solution
15 with large particle suspension is obtained, then a filtration process is required to remove particles larger than 1 μm from the solution provide that all necessary said components is present.

20 In accordance with this invention, setting process of the inorganic resin of present invention can be controlled by adjusting, such as, liquid/solid weight ratio, water content of the component A, granulometry of the wollastonite. The manner of changing these parameters,
25 whether alone or in combination may depend on various factors such as type of product desired and/or the type of equipment utilised. In accordance with this invention, the setting process can also be adjusted by curing temperatures. High temperatures will increase reactivity of the resin,
30 shorten setting process and produce more exothermic heat; on the other hand; low temperatures will reduce reactivity of the resin and prolong the setting process. This provides a large room for engineers to design and manufacture the composites based on inorganic resin of this invention, which
35 is not possible for the traditional phosphate cements. It can be noted that the true scope and spirit of this

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invention is to provide a unique composition with controllable pot life for the fresh mixture and good material properties for the hardened resin. This includes both quick setting and extended setting. The few minutes
5 setting time allows for quick repairing work, while the extended pot life permits to make composite materials using various available processing techniques.

In accordance with this invention, inorganic
10 resin composition may be fully cured at ambient temperatures within a limited duration. For example, at 20°C, the resin of this invention may be fully cured within 3 days in terms of developed strength and structural stability. Demoulding may however take place earlier, such as when the resin
15 finally sets. The resin can be cured in an open condition or closed condition, or in combination thereof. Usually the resin shows nearly no setting shrinkage when cured at ambient conditions, profile of any complicated configuration can be copied, and the resin products have a good surface
20 finish. The cured resin has a good resistance against water in terms of the dimension stability and chemical leaching, for instance, being immersed into water, pH value of the water keeps neutral, both the resin and the water is tasteless. Those properties are much similar to that of
25 organic polymer based resin, so that existing processing technique for organic and/or cement composite materials can be employed to make inorganic composite products based on this invention.

30 In principle, the resin products which are obtained do not require heat curing and may be placed in boiling water without adverse effect. The inorganic resin of the present invention can be placed in a desired configuration, the components interact and harden into a monolithic body with a
35 desired shape. However, curing and/or post curing at high temperatures and high pressures might be recommended to

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convert the resin into the final structures, when the resin products are destined for use at high temperature and/or in high pressure conditions. In general, the post curing process can further improve material properties of the
5 inorganic resin.

It is found that setting time of the fresh mixture of the present invention can be significantly prolonged at a temperature sufficiently low to retard any
10 setting reactions, so that the mixture remains viscous and/or gel like or as a slurry without setting. Being gradually heated up, such as to ambient temperatures, the resin of this invention will resume its reactivity and set without negative effects on its material properties. A
15 preferred method to practise this nature is to mix the resin composition and then keep the fresh mixture or slurry at the low temperatures. This nature provides a way to store the fresh resin for later use, it reduces waste and makes the resin easy to handle. By contacting the wollastonite
20 compound in the solution of phosphates with the oxy-boron compound for a sufficiently long time, large solid particles of the wollastonite may be decomposed, resulting in a slurry containing much smaller solid particles or even no discrete solid particles. The inorganic resin as a slurry treated at
25 a temperature sufficient low to prevent any setting reaction may be used as a matrix material to make a fibre reinforced composite or prepreg in which the fibres may be well impregnated. In practice, said slurry or said prepreg is then brought on a surface capable of supporting said slurry
30 or said prepreg respectively, the slurry reacting to set as a shaped product of the inorganic resin or said prepreg.

It is observed that the inorganic resin of the present invention has a very good adhesion to other
35 materials such as e.g., metals, organic and inorganic material such as the concrete based on the Portland cement.

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It has also good adhesion with fibres, such as, e.g., carbon fibres, organic fibres, such as e.g., polyester fibres, mineral fibres, such as, e.g., rockwool, metallic fibres and glass fibres, such as, e.g., E-glass fibres. The good
5 adhesion between fibre and matrix is essential for composite materials to impasse the load from matrix to the fibre, thus increase strength and stability of the composites. With these advantages, inorganic resins of this invention can be used to prepare composite materials reinforced by fibres,
10 such as, i.e., glass fibres.

Aggregate and refractory as long as they do not produce negative effect on material properties, preferably graded sand of mullite, silica, mica, cordierite, silicon
15 carbide, can be included in the dry blend in a controlled amount as filler to make the resin concrete of this invention, for improving performance and reducing cost of the resin product. Fillers can generally enhance the strength of the hardened resin product. Filler usage may
20 range up to about 90 percent by weight of the total composition. Other materials which can be used include particles of competent rocks or rock-forming minerals such as granite, basalt, dolomite, anesite, feldspar, amphibole, pyroxene, olivine, gabbro, rhyolite, syenite, diorite,
25 dolerite, peridotite, trachyte, obsidian, etc., as well as materials such as slag, fly ash of pulverised coal and that from corundum production, glass cullet, wood whips, and fibrous materials such as metal fibres, glass fibres, organic fibres and natural fibres. When intended to be used
30 at high temperatures, refractory fillers may employed, for instance, the refractory oxides, carbides, nitride, and silicides, such as aluminium oxide, lead oxide, chromic oxide, zirconium oxide or silicate, silica, silicon carbide, titanium nitride, molybdenum disilicide and carnonaceous
35 material such as graphite. In general, these fillers can be with different particle size, and can be both with cellular

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and non-cellular structures. Mixtures of the fillers can be used, when desired, including mixtures of metals and the ceramics.

5 Characteristically, hardened resin concrete of this invention is strong and durable. Toughness of the resin product can be achieved by adding fibres. The resin product of present invention has a good resistance against environmental attack, such as freezing(-20°C) /thawing(20°C)
10 cycles in terms of mechanical strength and dimension stability of the resin product. The resin product of present invention has also a good resistance against acid attack, such as H₂SO₄ solution of pH=1.5. Softening point of the inorganic resin itself is above 1100°C.

15 It is discovered that, surprisingly, articles based on the inorganic resin of the present invention has a very high surface scratch hardness when abrasion resistant fillers, such as, silicon carbide, boron carbide, corundum,
20 garnet, emery, silica and mixtures thereof, are used. The surface scratch hardness for the resin itself is about 6 Moh in wet and dry condition, but it can be significantly increased to 8.5 Moh or higher in dry condition, and 8 Moh or higher in wet condition when the abrasive grains are
25 included in the inorganic resin composition.

 In accordance with this invention, additives such as foaming agents and surfactants can be added to the freshly mixed inorganic resin so that shaped articles with
30 cellular structures with different bulk densities can be produced. In general, carbonates are the suitable species to produce uniform foaming of inorganic resin of this invention, although other foaming agents may also provide satisfactory results. Foaming is caused by CO₂ decomposed
35 from carbonates when contacting with acidic phosphate solutions. Carbonates such as MgCO₃, CaCO₃, ZnCO₃, Li₂CO₃

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and the like, or mixture thereof, which produce relatively insoluble phosphate can be used, with CaCO_3 and MgCO_3 being preferred. Other carbonates such as Na_2CO_3 and K_2CO_3 which produce relatively soluble phosphate salts may also be employed where leaching of the phosphate from the product in wet condition is not considered as a problem. The foaming agents can be added to the fresh resin of this invention at any moment before setting, however, they can also be premixed with the component C of this invention. Because the foaming is produced gradually, it is undesirable to have the setting prior to complete foaming. For that reason, this invention is very advantages over traditional phosphate cements to produce cellular structures because of the extended setting. Furthermore, because of the extended pot life, this invention leaves sufficient time to place the fresh mixture of the inorganic resin into any complex mould configuration, so that a foamed resin product with good surface finish can be obtained.

In accordance with this invention, surfactant which is not affected by phosphoric acids may be added into the resin to promote cell stability when making cellular structures. The surfactant may be premixed with the component C of this invention, or added to the freshly formed resin mixture before adding the foaming agent, so that the surfactant can be distributed homogeneously over whole volume of the composition. The surfactant might be, such as, e.g., zinc stearate.

Various pigments, both organic and inorganic as far as their coloring effect is not influenced by phosphoric acids and they have no negative effect on the inorganic resin of this invention, can be added to the resin to have colored resin products. The pigments can be used either as powder or liquid or in combination thereof.

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Generally, the inorganic resin of the present invention can be used as a binder both at low and high temperatures. In the field of composite materials, due to the controlled pot life and setting process, fibre reinforced composite can be produced using available material processing, such as, e.g., the hand lay-ups, the spray technique, the extrusion, the pultrusion and the hot pressing, wherein the resin impregnates the fibres and/or fibre mats to form a fibre reinforced product. The product based on inorganic resin of this invention can be strong and tough due both to the resin and function of fibres. The invention is generally applicable as inorganic binder to prepare, like but not limited, as coatings and/or surfacing agents such as e.g. fire resistance and corrosion resistance coatings; adhesives such as to bind metals and/or woods; special cements and concretes, such as dental material, with various characteristics, e.g., high strength and low leachate.

The inorganic resin of present invention can be applied indoors or outdoors to concrete drives, storage yards, warehouse and factory floors to repair and restore damaged surfaces. The resin can be used in the field of roadway construction, roadway patches and building reparation or other load bearing purposes. The characteristics of any particular concrete structures formed can depend on weight ratio of the various compounds, the nature of the aggregate employed, the curing conditions as well as other factors. Due to good adhesion between the inorganic resin of this invention and other cement products, such as that based on the Portland cement, the inorganic resin can be used to fill structure cracks in slabs, and repair highway median barrier walls. This resin can also be used in situation requiring in general a quick, permanent repair of concrete. The resin can be used to make pipes, ducts, moulded configurations in cellular and non-cellular

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structures; thermal, electrical and/or acoustical insulations; light weight products and the like because of its moisture resistance, high dielectric properties and cellular structures.

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The following experiments illustrate various embodiments of the invention. The amounts of the various constituents are given in parts by weight. Other embodiments will be apparent to one of ordinary skill in the art from a consideration of this specification or practice of the invention described therein. It is intended that the specification and experiments are considered as exemplary only, with the true scope and spirit of the invention being indicated by the claims which follow the examples.

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As an exemplary, a basic resin composition without additives in accordance with this invention is shown in Tab.1.

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Table 1

Component A*		Component B		Component C	
Fe ₂ O ₃	0.7	Na ₂ B ₄ O ₇ .10H ₂ O	6.0	Wollasto- nite	70.0
Al ₂ O ₃	4.3			Calcined wollasto- nite	30.0
ZrO ₂	6.3				
ZnO	13.1				
P ₂ O ₅	55.3				
H ₂ O	57.3				

* analytical result.

The component A, expressed by oxide according to oxide analysis, is prepared by dissolving Fe₂O₃, Zr(OH)₄, granular reagent grade zinc metal, and aluminium pellets in extra pure quality, together with balanced amount of water, in 85% orthophosphoric acid solution by mixing at about 90°C until a clear solution is obtained. This solution is kept at an ambient temperature of about 20°C for 6 months before

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use. The component B is $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, commonly known as borax. It is a dry powder with grain size less than 70 μm and in extra pure quality. The wollastonite of the component C has an aspect ratio of about 5, and 99.5 percent by weight of the wollastonite is not more than about 70 μm . Part of the wollastonite is calcined at 800°C and kept at 800°C for a duration sufficient to get all CaCO_3 decomposed to CaO and CO_2 .

In practice of this invention, the component A and component B are firstly pre-mixed together by a mechanical mixer at about 90°C for about 24 hours to form an aqueous solution. The wollastonite and calcined wollastonite in the component C are also pre-mixed, then added to above mentioned solution and mixed by a planetary mixer at about 20°C to form a fresh resin of this invention. The composition and procedure to prepare the resin of this invention will be referred as basic resin composition and basic preparation procedure hereafter.

Example 1

Examples of controlled pot life and initial setting time are shown in Tab.2.

Table 2

Component A	Component B $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	Component C	Pot life*	Initial set time
see Tab.1	0	see Tab.1	10 min.	20 min.
see Tab.1	2	see Tab.1	20 min.	1 hour
see Tab.1	4	see Tab.1	30 min.	10 hours
see Tab.1	6	see Tab.1	2.5 hours	17 hours
see Tab.1	10	see Tab.1	7 hours	24 hours

* the duration in which the resin keeps flowable

The fresh resin is formed by said basic resin composition and basic preparation procedure. Curing of said resin is at an ambient temperature of about 20°C in a covered condition. The results shown in the Tab.2 illustrate that pot life of

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the resin can be controlled so that both quick setting and extended setting of the resin can be obtained by addition of the component B. The pot life herein means the duration in which the fresh resin keeps flowable. The composition without the borax has a pot life of only 10 minutes which is too short to further add fillers or fibres, meanwhile the temperature of the mixture increases to more than 100°C during the reaction and it sets almost instantly. On the other hand, the resins of this invention induce less temperature increase and they are able to harden gradually. In general, more component B is used, less temperature increase, more extended pot life and longer initial setting will be. Further more, inorganic resins of this invention have good surface finish.

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Example 2

The inorganic resin has said basic inorganic resin composition and is made by said basic preparation procedure. This resin has a pot life of about 2.5 hours and initial setting of about 17 hours at 20°C in covered condition. The resin gets slightly warm during setting process with free water liberation but no noticeable setting shrinkage or expansion. Being cured at 20°C for 3 days in a covered condition, the specimen is demoulded and subjected to further drying or wetting before mechanical test. 3-points bending test shows that said resin has an average bending strength of 18.4 MPa, flexural modulus of 13.8 GPa when dried at 20°C for 3 days; bending strength 12.3 MPa and flexural modulus 12.0 GPa when immersed into water at 20°C for 3 days.

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Example 3

Two laminates are prepared by hand lay-ups. The matrix of the first laminate is the resin made from said basic resin composition and said basic preparation procedure, that of the second laminate is the polyester.

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Each of the laminates is made with 4 layers of the same unidirectional E-glass fibre mat. The laminates are cured at an ambient temperature of ca 20°C for 24 hrs in covered condition and then post cured at 60°C for another 24 hours in uncovered condition.

Table 3

Matrix	V_f vol %	Max strain %	Max load N	Modulus GPa measured	$E_f V_f$ GPa calculated
Inorganic resin*	14.0	1.90	7388.9	10.2	10.6
Polyester	22.6	1.91	8659.4	17.8	17.2

* Inorganic resin of this invention

Results of tensile test are shown in the Tab.3, where the strain is a mean value of the strain measured by strain gauge on both sides of the samples; the V_f is the fibre volume fraction, E_f is the modulus of the glass fibre, The $E_f V_f$ is calculated assuming $E_f=76$ GPa. It is observed that, for both laminates, their cracks are spreaded uniformly transversal to the fibre direction after the matrix break, and there is no delamination occurred before final rupture of the fibres.

Example 4

The resin has said basic composition and made by said basic preparation procedure. The hardened resin is subjected to the freezing(-20°C)/thawing(20°C) cycles for 30 times, the sample shows no noticeable dimension change and cracks.

Example 5

The resin has said basic composition and is made by said basic preparation procedure. Additional 200 parts by weight of mullite of 0-0.5 mm is added as filler. Curing is performed in a covered mould at an ambient temperature of

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20°C for 7 days, then demoulded and left uncovered in the ambient condition for 3 days. Scratch hardness on cut surface of the hardened resin is about 8.5, and there is no noticeable crack or dimension change when immersed in H₂SO₄ solution of pH=1.5 during 14 days.

Example 6

The resin has said basic composition and is made by said basic preparation procedure. The fresh resin is made at an ambient temperature of ca 20°C and then left at -20°C immediately. It remains flowable for several days and then gradually evolves to a gel without setting at -20°C.

Example 7

Composition of a foamed resin of this invention is shown in Tab.4, it is made by said basic preparation procedure. The surfactant is zinc stearate, the fibre is E-glass fibre. The MgCO₃ is added to the resin after other ingredients being mixed. Mixture of this composition foams gradually and sets at 20°C without applying external heat. The foamed resin is strong and it has a bulk density of about 350 kg/m³ and has uniform cell structures.

Table 4

Component A*		Component B		Component C		Additives	
Fe ₂ O ₃	0.7	Na ₂ B ₄ O ₇ .10H ₂ O	2.0	Wollasto- nite	100.0	MgCO ₃	5.0
Al ₂ O ₃	4.3					Surfac- tant	1.0
ZrO ₂	6.3					Talc	10.0
ZnO	13.1					Fibre	0.5
P ₂ O ₅	55.3						
H ₂ O	57.3						

*analytical result.

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Claims

1. An inorganic resin composition which comprises, in combination, an aqueous solution of metal phosphate (component A), an oxy-boron compound (component B) and a wollastonite compound (component C).

2. A composition according to claim 1 wherein the metal phosphate is selected from the group consisting of aluminium phosphates, zirconium phosphates, magnesium phosphates, zinc phosphates, calcium phosphates, iron phosphates, including derivatives and mixtures thereof.

3. A composition according to claim 1 or 2 wherein said oxy-boron compound is selected from the group consisting of boric acid, alkali metal and alkaline-earth metal salts of boric acid, amine and ammonium salts of boric acid, including hydrates and mixtures thereof.

4. A composition according to claim 3 wherein said oxy-boron compound is selected from the group consisting of boric acid, sodium borate, ammonium borate, calcium borate, including hydrates and mixtures thereof.

5. A composition according to claim 3 or 4 wherein said oxy-boron compound is as a powder or a liquid.

6. A composition according to claim 1 wherein said wollastonite compound is a natural or synthetic wollastonite, in calcined or non-calcined state, or a combination thereof.

7. A composition according to any one of claims 1 to 6 wherein said component A comprises, per 100 parts by weight of said wollastonite compound calculated on a basis of pure calcium silicate:

the equivalent of 14 to 135 parts by weight of phosphorous pentoxide contained in said metal phosphate, and the equivalent of 2 to 65 parts by weight of metal oxide contained in said metal phosphate.

8. A composition according to claim 7 wherein said component A comprises:

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the equivalent of 24 to 86 parts by weight of phosphorous pentoxide, and

the equivalent of 5 to 47 parts by weight of metal oxide.

5 9. A composition according to any one of claims 1 to 8 wherein the whole water content of the composition is from 8 to 150 parts by weight per 100 parts by weight of said wollastonite compound calculated on a basis of pure calcium silicate.

10 10. A composition according to claim 9 wherein the whole water content of the composition is from 11 to 95 parts by weight.

15 11. A composition according to any one of claims 1 to 10 wherein said oxy-boron compound is present, calculated on an anhydrous basis, in an amount of 0.2 to 50 parts by weight per 100 parts by weight of said wollastonite compound calculated on a basis of pure calcium silicate.

20 12. A composition according to claim 11 wherein said oxy-boron compound, calculated on an anhydrous basis, is present in an amount of 2 to 20 parts by weight.

 13. A composition according to any one of claims 6 to 12 wherein the particle size and the aspect ratio of the wollastonite are not larger than 150 μm and 10 respectively.

25 14. A composition according to any one of the claims 1 to 13 which comprises at least additives such as fibres, a filler, a foaming agent, a surfactant, and a pigment, used either alone or in combination thereof.

30 15. A composition according to claim 14 wherein said surfactant is zinc stearate.

 16. A composition according to claim 14 or 15 wherein said foaming agent is a carbonate selected from the group consisting of calcium carbonate, magnesium carbonate, sodium carbonate, potassium carbonate, used either as powder
35 or aqueous solution, or a combination thereof.

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17. A composition according to any one of claims 14 to 16 wherein said filler is silica or a derivative thereof.

18. A composition according to any one of claims 14 to 17 wherein said fibre is selected from the group consisting of metal fibre, organic fibre, and inorganic fibre including glass fibre.

19. A process for preparing said aqueous solution of metal phosphate of said composition according to any one of claims 1 to 18 which comprises mixing metal and/or metal oxide and/or metal phosphate including hydrates and derivatives thereof in phosphoric acid aqueous solution at a temperature and for a time sufficient to form at least a semi-transparent solution.

20. A process for preparing a product of the inorganic resin composition according to any one of claims 1 to 19, which comprises:

mixing said aqueous solution of metal phosphate with said oxy-boron compound at a temperature and for a time sufficient to form an aqueous solution, and

contacting said wollastonite compound and optionally one or more of said additives with the above solution to form a slurry, and

bringing said slurry on a surface capable of at least partially supporting said slurry wherein said slurry reacts to set as a shaped product of the inorganic resin composition.

21. A process for preparing a prepreg product of said inorganic resin composition according to any one of claims 1 to 19, which comprises:

mixing said component A, said component B, said component C and optionally one or more of said additives to form a slurry, and

impregnating fibres with said slurry, and

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keeping the impregnated fibres, which is called prepreg, at a temperature sufficiently low to prevent any setting reaction, and

bringing said prepreg on a surface capable of supporting
5 said prepreg wherein the slurry reacts to set as a shaped product of said prepreg.

22. A process according to claim 20 or 21 wherein said slurry is kept at a temperature sufficiently low to retard any setting reaction before being brought on
10 said supporting surface.

23. A process according to any one of claims 20 to 22 wherein said supporting surface comprises fibres including inorganic, organic and/or metallic fibres.

24. A process according to any one of claims 20
15 to 23 wherein said slurry impregnates said fibres of said supporting surface to form a fibre reinforced product.

25. A process according to any one of claims 20 to 22 wherein said supporting surface is made of metal, organic, or inorganic material.

20 26. Use of an inorganic resin composition according to any one of claims 1 to 19 and/or a shaped product of the inorganic resin composition prepared by the process according to any one of claims 20 to 25, as a binder, coating, surfacing agent, adhesive, cementing agent.

25 27. Use according to claim 26 wherein the shaped product has a foamed structure.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/BE 95/00106

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C04B28/34 //(C04B28/34,14:04,20:00,24:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,23 56 524 (C. WÜSTEFELD) 28 May 1975 see page 5, line 31 - page 6, line 3 see page 7, line 16 - page 8, line 13 see claims 1,4-6,11 ---	1-6,14, 26
A	DE,A,30 43 856 (ZSCHIRMER & SCHWARZ) 3 June 1982 see claims 1-5 ---	1-5,14, 17,26
A	FR,A,2 291 951 (W.R.GRACE & CO.) 18 June 1976 see page 2, line 10 - line 28 see claims 1,3,4 --- -/-	1-5,14, 17,26

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/BE 95/00106

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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